

ABSTRACT

In recent year, photocatalyst has been gaining a wide attention as the ability to harness the free energy from sunlight to perform variety of function such as organic degradation, solar cell and etc. When used as photocatalyst, titanium dioxide (TiO_2) is able to absorb ultraviolet light only (UV) to initiate the oxidation and reduction which is able to speed up the degradation of dye. This thus provides a cheap and efficient method to solve the dye mismanagement that is face in industries these days. In this work, the titanium dioxide nanoparticle is modified via hydrazine wet method to increase photocatalytic activity. The photocatalytic activity is studied via methylene blue degradation, followed by the kinetic study on the methylene blue degradation. The catalyst has been characterized via UV-VIS spectrophotometer, FTIR machine and XRD machine. From the result, we realized that the main reaction that occurred during the modification is combustion of hydrazine on the surface of TiO_2 . From the UV-Vis spectrum, we found out that the modify catalyst can absorb more visible light as compare to the commercial TiO_2 . FTIR spectrum indicated that NH_x group, NO group and an increase of OH group is presented after the modification. XRD pattern analysis suggested the crystallinity of the catalyst is slightly increased after the modification. Methylene blue degradation also showed that the modified catalyst have a higher activity as compared to the commercial one. The results obtained suggesting that the photocatalytic activity is increasing due to the ability of the catalyst to absorb visible light after the treatment. The modeling is done by relating the rate of methylene blue degradation with the direct hole attack and the hydroxyl radical attack occurred in the reaction.

ABSTRAK

Di kian hari, keupayaan fotokatalis untuk mempergunakan tenaga matahari untuk melakukan pelbagai aktiviti seperti degradasi pewarna, sel solar dan sebagainya telah menerima perhatian dari pelbagai pihak. Apabila digunakan sebagai fotokatalis, TiO_2 dapat menyerap tenaga cahaya ultraungu (UV) untuk memulakan proses pengoksidaan dan reduksi, di mana proses ini adalah berfaedah untuk mempercepatkan proses degradasi pewarna. Keupayaan ini telah menyumbangkan idea untuk menyelesaikan masalah pengendalian pewarna yang dihadapi oleh pihak industri baru-baru ini. Dalam kertas ini, TiO_2 telah dimodifikasi menggunakan teknik kebasahan hydrazin untuk meningkatkan fotoaktiviti pemangkin tersebut. Fotoaktiviti pemangkin adalah dikaji melalui degradasi biru metilena, diikuti oleh kajian kinetik terhadap reaksi tersebut. Sifat-sifat pemangkin adalah diperoleh melalui spektrofotometer UV-VIS, mesin FTIR dan mesin XRD. Melalui eksperimen, ianya didapati bahawa reaksi yang berlaku semasa modifikasi berlaku adalah pembakaran hydrazin di atas permukaan TiO_2 . Melalui keputusan yang diperoleh, pemangkin yang dimodifikasi berupaya untuk menyerap lebih banyak cahaya ketara berbanding dengan pemangkin komersial. Spektrum FTIR mencadangkan kumpulan NH_x dan NO , diikuti oleh penambahan kumpulan OH telah muncul di atas pemangkin selepas berlakunya modifikasi. Spektra XRD juga menunjukkan peningkatan kristaliniti dalam pemangkin selepas berlakunya modifikasi. Ujian degradasi biru metilena juga menunjukkan pemangkin yang dimodifikasi menunjukkan fotoaktiviti yang tinggi berbanding pemangkin komersial. Keputusan ini telah menunjukkan terdapat peningkatan fotoaktiviti dalam pemangkin yang telah dimodifikasi adalah disebabkan oleh keupayaan pemangkin untuk menyerap cahaya ketara selepas dimodifikasi. Pemodalan reaksi telah dibuat dengan mengaitkan kadar degradasi biru metilena dengan serangan lubang berketerusan dan serangan hidroksil radikal yang berlaku dalam reaksi tersebut.

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LIST OF ABBREVIATIONS

<i>Abbreviation</i>	<i>Definition</i>
N-TiO ₂ -60	Commercial catalyst treated at 60°C
N-TiO ₂ -110	Commercial catalyst treated at 110°C
N-TiO ₂ -170	Commercial catalyst treated at 170°C
XRD	X-Ray Diffraction
FTIR	Fourier Transform Infra-Red
UV-Vis	Ultraviolet/Visible
MB	Methylene Blue
XPS	X-ray Photoelectron Spectroscopy
QSSA	Quasi Steady State Assumption

1 INTRODUCTION

1.1 *Overview*

Photo-catalyst is one of a kind catalyst which utilizing light to play a part in modify the rates of photo-reaction. Photo-catalyst has the ability to initiate oxidation and reduction process when the light is illuminated on the surface of the catalyst due to the existence of the band gap in the semiconductor, which differ them from the normal catalyst which depending on the adsorption, surface reaction and the desorption of the surrounding molecule to improve rate of reaction. When the electron in the valance band has absorbed photon from a particular wavelength, the electron in the valance band will be excited to the conduction band, leaving a hole in the valance band. Later on, the electrons on the conduction band will move to surface of the catalyst to initiate reduction process, while the holes at the valance band will move to surface to initiate oxidation process. So far semiconductor like TiO_2 is proven better in terms of cost, stability and performance compare to other semiconductor, still the large band gap in TiO_2 (3.2eV) causing the catalyst can absorb only UV light and only can work in near UV range visible light only (Jiang et al, 2012). This cause the application of TiO_2 inconvenient and costly as another UV source is needed to enable the function of TiO_2 . At the same time, sunlight at the top of Earth's atmosphere consisted of about 50% infrared light, 40% visible light and 10% UV light (Qiang Fu, 2003). So it is desired that TiO_2 is modified to be able to absorb those lights from the sun itself.

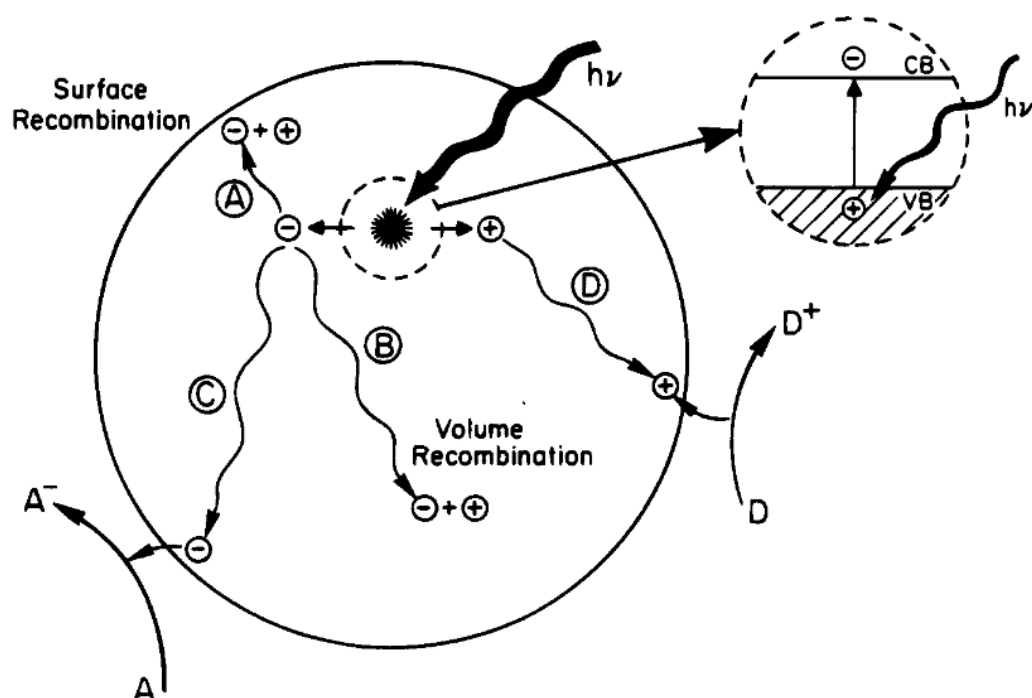


Figure 1.1: Schematic diagram on photoexcitation and the deexcitation phenomena in photocatalyst (Linsebigler et al, 1995)

1.2 Background of the Proposed Study

Large amounts of colored wastewater are generated in industries which use dye such as methylene blue to give the desired color to their product. Still these dye is mismanaged and has been discharged into environment especially river without adequate control, resulting negative impact to the environment and to the human health (Zolinger et al, 1991). The presence of dye in in the natural stream can harm the aquatic life by increasing the toxicity and chemical oxygen demand, and impeding photosynthetic phenomena through reduction of light penetration (Bulut et al, 2006). So far, methods that are used to treat the dye are adsorption, electrocoagulation, ultrasonic decomposition, advance chemical oxidation, nanofiltration, and chemical coagulation followed by sedimentation were implemented to remove dyes from wastewater (Sannino et al, 2013). In recent year photocatalytic degradation with TiO_2 under visible light is gaining more attention in industry and academic. This is so as this method of treatment is much cost effective

as compared to method that is used currently; where sophisticated equipment is to be used in order to treat the dye. While with the proposed method, only few things are needed for the treatment: a reactor, a mixer, the catalyst and the sunlight.

1.3 Problem Statements

In order to create the TiO_2 that is much more active in visible light, one method that is studied the most so far is doping nitrogen into the lattice of TiO_2 . So far there are various ways to dope the nitrogen into the lattice of TiO_2 such as sol-gel method, reaction of TiO_2 with N- containing species such as ammonia, urea and etc, plasma treatment method, and oxidation of Ti-N film to TiO_2 -N film. Still usually all these methods is not cost effective for bulk production as the preparation usually involving sophisticated equipment and high temperature, especially the plasma treatment method involving creation of nitrogen in plasma form at temperature at 400°C in a plasma chamber (Chen et al, 2007).

So far, wet hydrazine treatment method has been showing a promising way to prepare an N-doped TiO_2 (Li et al, 2007; Selvam et al, 2012). The modification process is done where the TiO_2 powder is immersed in hydrazine hydrate (80%) for 12 hour, filtered and dried with air at 110°C . The simplicity of the process, the unnecessary of using harsh condition, and the needless of calcination making this treatment interesting as it is possible to convert the lab scale production of this catalyst to a larger scale with a minimum cost. Still the reaction that is occurred during the modification is still not fully understood.

1.4 Research Objective

The objective of the research is:

- 1) To synthesis N- TiO_2 that absorbs light in visible region using wet hydrazine method.
- 2) To inspect the photoactivity of the modified TiO_2 .
- 3) To model the methylene blue degradation reaction.

1.5 Research Question/ Hypotheses

Q1 What is the reaction involved in the wet hydrazine method?

H1 Hydrazine is an active chemical which can be burned at air at relative low temperature with a strong heat release (621.74kJ/mol) (Rane et al, 2007). It is speculated that ignitability of the hydrazine is the one that responsible for the nitrogen to be doped into the TiO₂ (Li et al, 2007). This speculated is associated with Li et al (2007) and Selvam et al (2012) respectively when a glow is actually detected on the surface of the catalyst when the TiO₂ and the hydrazine hydrate (80%) mixture is dried in air at 110°C, turning the color of the catalyst from white to yellow color. So we hypothesize that the reaction that happened during the drying process is the combustion process. Still the exact temperature of the combustion to happen is still remaining unknown.

Q2 Is there another reaction happened between TiO₂ and hydrazine?

H2 According to Chung et al studies in 2000, it is found out that at 35°C, an isolated hydroxyl group and several nitrogen species is bonded on TiO₂ when the gas hydrazine is exposed on the surface of TiO₂. When the temperature is increasing to 150°C, the isolated hydroxyl group is decreasing along with the increment of temperature. But when the temperature is raised from 150°C to 200°C, the N₂H₄ adsorbed on the TiO₂ is further decompose to other N species or desorbed from the catalyst. At the same time the isolated hydroxyl adsorption in the range 3600-3800cm⁻¹ is further enhanced along with this increment of temperature in this range. So with this, we can hypothesize that during the mixing, there is another reaction indeed happened besides the combustion of hydrazine as mentioned above.

1.6 Scope

This research will be focused on examine the effect of the drying temperature towards the catalyst itself. The effects that are concern is the properties of the catalyst such as the light absorption, phase of catalyst, species presented in the

catalyst, and the photocatalytic activity of the catalyst itself. For light absorption of the catalyst, the properties will be studied using UV-Vis Spectrophotometer. For the phase of catalyst, it will be studied using X-Ray Diffraction Machine. As to determine the species presented in the catalyst, FTIR analysis is performed to infer the species appeared in the catalyst. As for the photocatalytic activity studies, the methylene blue degradation studies has been conducted to check the photoactivity of the catalyst itself. Besides that, the kinetic study on the methylene blue degradation for the after modified TiO_2 is examined also in this project.

1.7 Expected Outcome

The expected outcomes of the research are:

- 1) The nitrogen is successfully doped inside the TiO_2 lattice via hydrazine combustion.
- 2) The photocatalytic activity of the N- TiO_2 is increased compared to the commercial TiO_2 due to the increase of the visible light absorption of the N- TiO_2 .
- 3) The modeling on the methylene blue degradation with the modified catalyst is done.

1.8 Significance of the Proposed Study

With this study, a simplified method to create the catalyst will be more understood, especially on the reaction involved during the procedure that responsible to the doping of the nitrogen into the catalyst. By understanding the reaction occurred during the treatment, the bulk production of the catalyst will be possible by identifying and minimizing several vital variable as to make the method to be cost effective. With the modeling on the modified catalyst is done, the design equation for the photocatalytic reactor is available, making the volume design of the photocatalytic reactor is possible.

2 LITERATURE REVIEW

2.1 *Introduction*

Photo-catalyst is one of a kind catalyst which utilizing light to play a part in speeding up the reaction by initiating oxidation and reduction process when the light is illuminated on the surface of the catalyst. TiO_2 is proven better in terms of cost, stability and performance compare to other semiconductor, still the large band gap in TiO_2 (3.2eV) causing the catalyst can absorb only UV light and only can work in near UV range visible light only (Jiang et al, 2012). This cause the application of TiO_2 inconvenient and costly as another UV source is needed to enable the function of TiO_2 . Up until now, most researches have been focused on reducing the band gap of the semiconductor, in hoping that by reducing the band gap, TiO_2 is able to absorb the light from the visible range, thus improving the photoactivity of the catalyst itself. Here several strategies on how to reduce the band gap of the TiO_2 has been reviewed such as the creation of Ti^{3+} defect site, oxygen vacancy, surface disordered layer, and nitrogen doping. Later on, the literature review is also done on the relation to be used in the modeling of the methylene blue degradation.

2.2 *Ti^{3+} Defect Site, Oxygen Vacancy and Surface Disordered Layer*

In 2011, Chen et al reported a disorder-engineered TiO_2 nano-crystal which able to produce hydrogen via water splitting under sunlight. In the work, the prepared catalyst made is annealed in a very rough condition of 200°C with 20bar hydrogen for 5 days, results a black colored TiO_2 . Wang et al (2011) work on treating TiO_2 nanowire with hydrogen gas is only able to improve the UV light absorption, but still unable to convert the photon to current under the incident wavelength above 430nm. Using Helium gas as the inert gas for thermal treatment at 400°C for 3 hour for 3 phases of TiO_2 , Liu et al (2012) also get a similar result where the UV light absorption is improve but not able to absorb light in visible region.

It has been acknowledged that thermal annealing can create a Ti^{3+} defect site, or oxygen vacancies on the TiO_2 surface (Lu et al, 1994). This also can be done by annealing in a reducing atmosphere where the oxidation is prevented by introducing inert gas like hydrogen and helium (Xiong et al, 2011). In Wang et al (2011) work, the photo-activity enhancement in the UV region can be attributed to the increased electron donor density which is left by oxygen vacancies. While in Liu et al (2012) work, the Ti^{3+} defect sites is functioned as reactive sites for the adsorption of reactants and allow the effective charge or hole transfer between the reactant and the surface of the semiconductor. Lu et al (1994) also mention similar things where the oxygen vacant at bridging-O site leaves two Ti^{3+} exposed, making TiO_2 surface more reactive than other oxides such as Al_2O_3 and SiO_2 , and affecting the dissociative chemisorption of molecules such as H_2O , NH_3 and etc.

Oxygen vacancies are also being responsible for visible light absorption (Xiong et al, 2011). It is believed that oxygen vacancy creates surface states in the forbidden band gap with energy 0.75 to 1.18eV below the conduction band minimum of TiO_2 (Cronmeyer, 1959). Wang et al (2011) suggested that the visible light is possible due to the transitions from the TiO_2 valance band to the oxygen vacancy state, or from the oxygen vacancies states to the conduction band since both ways require less energy for excitation. Here they hypothesize that the reason why their photo-catalyst couldn't absorb visible light is due both oxygen vacancy state is well below the redox potential of $\text{H}_2\text{O}/\text{H}_2$. Another hypothesis proposed is that the electronic transition between localized vacancy state and the delocalized conduction band is not significance as the coupling between both states should be weak. Still no UV-vis spectrophotometer is done to check whether the catalyst itself is able to absorb the visible light.

Zuo et al (2010), with the aim to create a Ti^{3+} photo-catalyst via combustion method is able to absorb incident wavelength up until 700nm and above and reducing water to hydrogen gas under incident light with wavelength 400nm and above. The formation of the Ti^{3+} in the bulk is verified by Electron Paramagnetic Resonance (EPR) spectra. From EPR and X-ray Photoelectron Spectroscopy (XPS) study also, they confirmed that the Ti^{3+} is presented in the bulk of the catalyst instead on the surface of the catalyst. The Plane-Wave Self-Consistent Field (PWscf)

simulation also reveals that a mini band is rising up closely below the conduction band minimum, which is in agreement with Cronemeyer (1959) findings. They also realize that the width of the vacancy band is directly proportional to the concentration of the vacancy too. The success of the absorption of visible and infrared light can be contributed by creating Ti^{3+} in the bulk TiO_2 rather than on the surface. If the Ti^{3+} is created on the surface, the surrounding oxygen will be absorbed by Ti^{3+} , eliminating the oxygen vacancy and hence the surface state in the band gap. Wei et al (2012) also created Ti^{3+} in the bulk TiO_2 via hydrogenation, reporting wavelength absorption up until 1800nm as verified by UV-is diffuse reflectance spectra, signifying the importance of Ti^{3+} in the bulk to enabling the function of Ti^{3+} to absorb sunlight.

Examining the work by Chen et al (2011), one obvious difference between their works and the others is the objective to create a disorder engineered TiO_2 , with the TiO_2 Nano-crystal as the core and the highly disordered layer as the shell, instead of creating a Ti^{3+} based TiO_2 . In his work, the role of the disordered layer is to create mid-gap states. Mid-gap states or band tail states can form a continuum extending to and overlapping with the conduction band edge and the valance band, hence narrowing the band gap from 3.3eV to 1.54eV. This narrowing enabling the photocatalyst to absorb simulated solar light ranging from 550nm to 700nm in methylene blue solution. Naldoni et al (2012) also obtained a similar result by creating the crystalline core/ disordered shell TiO_2 where the band gap is narrowed from 3.25eV to 1.85eV. At the same time, they also found out that their catalyst containing Ti^{3+} in the bulk; possess two oxygen vacancy surface states, therefore contributing in light absorption in the same way as mentioned by Wang et al (2011).

In Chen et al (2011) works, they found out that after hydrogenation, one H atom is bonded to an O atom while another atom is bonded to a Ti atom. This suggests that the source of the black color TiO_2 and the formation of the disordered layer are due to the formation of this crystal structure on TiO_2 . Similar findings also reported by Wei et al (2011), where the formation of the Ti-H and O-H is founded on the surface of the TiO_2 , contributing to the band gap narrowing besides the formation of Ti^{3+} in the bulk catalyst.

Still, there seems to be no a parallel pattern on how this surface disorder are created so far. In Chen et al (2011) work, the as-prepared TiO_2 powder is calcinated at 500°C for 6 hour to improve the crystallinity of TiO_2 . Later on the TiO_2 is heat treated in the chamber by hydrogenation at 20bar at 200°C for 5 days to obtain black TiO_2 . In Naldoni et al (2012) work, the TiO_2 first is treated under vacuum and then heated at 200°C under O_2 flow for 1 hr. After the sample is cooled to room temperature, the TiO_2 is reduced in 500°C under H_2 flow in 1 hr to obtain black TiO_2 . In Wei et al (2011) work, the as prepared TiO_2 is treated with hydrogen in 10bar pressure, at 200°C for 2 hr, yielding a dark blue TiO_2 . In Wang et al (2011) work, the as prepared TiO_2 nanowire were 1st annealed in air for 3 hr, followed by hydrogen treatment at various temperature (200°C to 550°C) for 30 minute. The TiO_2 is founded to turn black at temperature 450°C . Still, they reported that the valance band of the catalyst is remaining unchanged after treating with hydrogen, suggesting that the black color of the TiO_2 is entirely due to the point defect like oxygen vacancy (Diebold, 2004).

2.3 Nitrogen Doping TiO_2

In 2001, Asahi et al reported about the N- TiO_2 where the band gap of the catalyst is founded to shift dramatically from the UV region to the visible light region from their absorption spectrum by sputtering TiO_2 into the N_2/Ar gas mixture. And it is also shown that due to this factor, the photo activity of the catalyst itself is also remarkably enhanced due to this factor. Since then, nitrogen doping has been receiving a lot of attention up until now. So far, several methods have been proposed around on the way to introduced nitrogen into TiO_2 such as:

- 1) Sol Gel Method (Livraghi et al, 2006), where the titanium dioxide pre-cursor is mix with N containing chemical to yield the $\text{TiO}_2\text{-N}$.
- 2) Reaction of TiO_2 with N-containing chemicals such as ammonia instead of nitrogen (Asahi et al, 2001).
- 3) Plasma Treatment Method (Chen et al, 2007), where the nitrogen is introduced into the TiO_2 by converting the nitrogen gas into plasma form.

4) Oxidizing the Ti-N film into TiO₂-N film (Zhu et al, 2010).

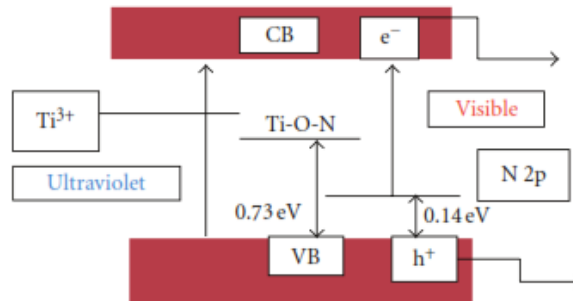


Figure 2.1: Formation of mid gap at forbidden band gap caused by Ti-O-N and chemisorb N in TiO₂ (Viswanathan et al, 2012).

Beside Asahi, several research groups (Irie et al, 2003; Sato, 1986; Beranek et al, 2007) also reporting that doping nitrogen into TiO₂ indeed has shifted the semiconductor from UV region to visible light region regardless of any method used to introduce N into the semiconductor, followed by the increasing of photo activity of the catalyst. As to explain the shift of absorption spectrum from UV region to visible region, Asahi et al proposed that the introduction of the mid gap caused by formation of Ti-O-N bond and the chemisorbed N₂ in the forbidden band gap. Another proposal has been suggested by Emeline et al (2007) where the reason for the visible light absorption is due to the formation of the oxygen vacancy and the Ti³⁺ in the TiO₂ lattice, while the function of N is to stabilize these defect only.

To proof the presence the existence of Ti-O-N bond and the chemisorbed N₂ in TiO₂ lattice, evidence is presented through the XPS analysis showing peaks at 396eV, 400eV and 402eV correspond to nitrogen N1s core level. It is proclaim that the N⁻, or the Ti-O-N is being responsible for the peak 396eV while the chemisorbed N₂ is responsible to the peak 400eV and 402eV. These XPS analysis result also is supported by Viswanaten et al (2012), which had done a detailed review regarding the XPS results of N-TiO₂ catalyst collected from around the research group. According to Viswanaten et al (2012), although there is no consensus among the

results and researchers about the species assignment of the nitrogen 1s binding energy in N-TiO₂ catalyst up until now, still the group has concluded several rules of thumb that are helpful when analyzing the XPS results:

a) If N⁻ is present in the catalyst, then the valance state of Ti has to be different from Ti⁴⁺.

b) N-1s-binding energy will normally appeared in the range 396-397eV when the nitrogen content in the system is very small. When the nitrogen content in the system is high, the higher binding energy (about 400eV) peak will appear also. This peak is considered as the chemisorbed nitrogen species on the catalyst surface in general.

c) The acceptable binding energy value of N 1s level in the substitute system is around 396-397eV. If the nitrogen is in anionic state, then the nitrogen-1s binding energy should be around 394eV. While if the nitrogen is in cationic state, the binding energy of the species should be around 400eV. Still this reading is unlikely to happen on the basis of the size and charge of the cation itself.

2.4 Hydrazine Wet Method

In 2007, Li et al has proposed a new way to synthesis the TiO₂-N using a very simple method, which is call the hydrazine method. In this method, the white powder TiO₂ is dipped in hydrazine hydrate (80%) for 12hr. The solution is then filtered and dried at 110°C for 3 hours in air. The end product resulted a yellow color nitrogen doped TiO₂. Throughout this method, they successfully created a yellow N-TiO₂, where the light reflectance spectrum showing that the catalyst has shifted clearly from UV region to visible light region. The photoactivity test which is done via photocatalytic oxidation of ethylene into carbon dioxide also clearly indicates that the catalyst is able to boost the conversion of ethylene 0.5% to 9.5%.

During his experiment, Li et al (2007) realized that during the drying process, a glow is detected after evaporating a few solutions from the surface. Once the glow occurred, the catalyst is turned into yellow color. In 2012, Selvam et al also reported the same thing when they are using the exact same method to treat the TiO₂ pre-treated with combustion solution technique, where the glow is detected also during

the drying process and the catalyst becoming yellow after that. This lead the group to believe that during the drying process, combustion is occurred between hydrazine and the oxygen at 110 °C. In 2007, Rane et al has prepared their N-TiO₂ via sol gel method by utilizing hydrazine hydrate (99%) as the precursor. Here they mentioned that when the hydrazine exposed at lower temperature will reacts with the oxygen in the atmosphere as follows:



The glow that is detectable from eyesight can be due to the large amount of heat is liberated when the hydrazine is combusted. Rane et al (2007) also mentioned that in his reaction, the nitrogen that is formed by the combustion of hydrazine gets trapped in the lattice of TiO₂, yielding a yellow color nitrogen doped TiO₂. Hence from these 3 research group, we hypothesize that during the reaction, the hydrazine is combusted with the oxygen at 110°C to give nitrogen and water. When the nitrogen is produced, the nitrogen will introduce into the TiO₂ with the help of enormous amount of heat that is released during the hydrazine combustion.

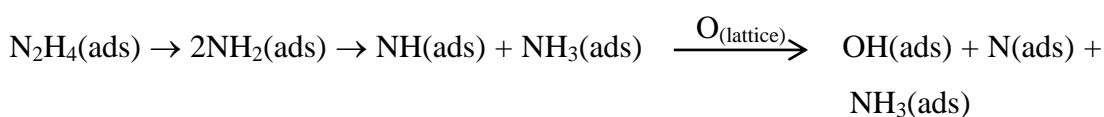
As to evidence that the nitrogen is successfully doped into the TiO₂ lattice, Li et al (2007) and Selvam et al (2012) has done XPS analysis on their samples. As for Li et al, a peak is found at 396.6eV from the XPS spectra for N1s core level. Li et al believe that this peak is correspond to Ti-N bond, which is the main reason on why the catalyst able to absorb the visible light. As for Selvam et al, a peak is found at 398.1eV from XPS spectra for N1s core level. Here they justify that this peak is assigned to anionic N in the Ti-O-N bond. Although both XPS analysis resulting different binding energy so far, still one thing can be confirm is that this combustion process is able to introduce nitrogen into TiO₂ lattice.

As to investigate whether this combustion will damage or alter the surface of the catalyst, the X-Ray Diffraction (XRD) analysis has been performed. From Li et al (2007) result, it can be seen that after the hydrazine combustion, the main peak of anatase phase at $2\theta=25.4^\circ$ is far sharper than the pretreated TiO₂. This shows that via the spontaneous combustion of hydrazine on the surface of TiO₂, the crystallization of TiO₂ has becoming better. Thus Li et al (2007) also proclaim them via this method; no further calcination is needed as the catalyst is already in the anatase

phase. While from Selvam et al (2012), the phase of TiO₂ after undergoing hydrazine treatment is in anatase since a significant sharp peak is shown at 25.43°. Although the phase of the TiO₂ is already in anatase phase after the solution combustion technique, still one thing that can be proven here is that via this method, the phase of the TiO₂ will not be revert back from anatase to rutile phase. This is vital as it is evidence that the surface configuration of anatase phase TiO₂ can help in improving the photocatalytic activity of the catalyst itself (Diebold et al, 2004).

2.4.1 Interaction of Hydrazine with TiO₂

One thing worth mentioned here is the studies conducted by Chuang et al (2000) on the interaction of hydrazine on TiO₂ using Infra-Red (IR) spectroscopy studies. In this study, the TiO₂ is mounted inside the IR cell for FTIR spectrum analysis. Later on, N₂H₄ gas is introduced into the IR chamber at various temperatures. From the studies, it is found out that at 35°C, an isolated hydroxyl group and several nitrogen species is bonded on TiO₂. When the temperature is increasing to 150°C, the isolated hydroxyl group is decreasing along with the increment of temperature. But when the temperature is raised from 150°C to 200°C, the N₂H₄ adsorbed on the TiO₂ is further decompose to other N species or desorbed from the catalyst. At the same time the isolated hydroxyl adsorption in the range 3600-3800cm⁻¹ is further enhanced along with this increment of temperature in this range. From here, a mechanism has been proposed to fit the result obtain from the FTIR as follows:



Here the adsorbed N₂H₄ is decomposed to NH and NH₃ first. Then later on when the temperature is around 150°C to 200°C, the NH adsorbs will further decomposed to donate hydrogen atom to surface lattice oxygen atoms, generating OH and N adsorbed on the catalyst. One interesting fact to be found here is that the formation of the OH bond on the surface of the catalyst. As mentioned in previous section, one of the main factors that contribute to the band gap reduction is the formation of Ti-H bond that created the oxygen vacancy and the surface disorder as reported by Chen et

al (2011). Since there is no research reporting the catalyst with O-H bond, so it will be interesting to see the effect of this species on the photoactivity of the catalyst itself.

2.5 *Methylene Blue Degradation Modeling*

Here the reaction modeling of the methylene blue degradation modeling will be reviewed. The modeling is done as to characterize the reaction itself with an equation so that the reaction can be predictable under various operating condition. This modeling is important also as to provide the design equation to design the photocatalytic reactor, where the equation on the rate of reaction is needed in order to design the volume of the continuous reactor or the reaction time as for the batch reactor.

In 2013, a model has been proposed by Sannino et al (2013) to model a reaction considering the concentration of the methylene blue at that time, the intensity of the light and the weight of the catalyst used. Hence a methylene blue mass balance has been written as follows:

$$V \cdot \frac{dC(t)}{dt} = r(C, I) \cdot W_{TD}$$

Here the V is the solution volume (L). $C(t)$ is the methylene blue concentration (mgL^{-1}). r is the reaction rate ($\text{gL}^{-1}\text{min}^{-1}$). W_{TD} is the catalyst amount (g). And I is the light intensity reaching the catalyst surface (mWcm^{-2}).

Later on, the mass balance is further modelling the methylene blue concentration and the intensity of the light with the Langmuir-Hinshelwood mechanism rate law. Then, the Lambert-Beer law is used to further modelling the intensity of the light in the form Langmuir-Hinshelwood mechanism rate law again as to consider the screening effect, where the penetration of light decreases when the catalyst loading is increasing. Hence, the rate of degradation of methylene blue is written as follows:

$$V \cdot \frac{dC(t)}{dt} = -K_1 \cdot \frac{b \cdot C(t)}{1 + b \cdot C(t)} \cdot \frac{\alpha \cdot I_0 \cdot e^{-k_1 \cdot [\text{TiO}_2]}}{1 + \alpha \cdot I_0 \cdot e^{-k_1 \cdot [\text{TiO}_2]}} \cdot W_{\text{TD}}$$

Where:

K_1 = Kinetic constant ($\text{mg g}^{-1} \text{min}^{-1}$)

α = Light absorption coefficient ($\text{cm}^2(\text{mW})^{-1}$)

k_1 = Specific extinction coefficient per unit catalyst mass (L mg^{-1})

I_0 = Light intensity incident on the reactor surface (mW cm^{-2})

$[\text{TiO}_2]$ = Catalyst dosage (mg L^{-1})

b = Adsorption coefficient (L mg^{-1})

Still several weaknesses have been detected within this model. As mentioned before, the intensity of the light here has been modelled referring to Langmuir-Hinshelwood mechanism rate law. As known, this Langmuir-Hinshelwood mechanism rate law is usually used to describe the reaction pathway of a catalytic reaction, where the reaction between two atoms is occurred when they are adsorbed on the surface of the catalyst as depicted as follows: